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Cast polyurethanes obtained from reactive recovered polyol intermediates via crude glycerine decomposition process

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Abstract

In this work, the possibility of applying intermediates from polyurethane waste recycling in polyurethane synthesis was presented. Polyurethanes were synthesised in a two-step method using a mixture of petrochemical polyol and glycerolysate as a reactive component and 4,4-diphenylmethane diisocyanate (MDI). Glycerolysates were produced during decomposition of polyurethane elastomer by crude glycerine from biodiesel production. The glycerolysates were incorporated into polyurethane structure and co-created a soft segment with their functional groups. Chemical structure and properties of the cast polyurethanes were characterised by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and mechanical tests. Results showed that higher incorporation of glycerolysates shifts the glass transition to higher temperatures and the mechanical properties indicates that material exhibits more stiff structure. Prepared polyurethanes which contained glycerolysates have good and similar (in a small amount of glycerolysate) properties to the reference polyurethane which indicates the possibility of glycerolysate application as a polyol in the polyurethane synthesis.

Keywords: Polyurethane elastomer; chemical recycling; crude glycerol; thermal characterisation, mechanical properties

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1. Introduction

Polyurethanes (PUs) are a group of plastics that can be produced from the wide spectrum of substrates, and that can be submitted on obtaining a various structure with different structure and ipso facto on the final application of these materials. Hence PUs found many uses in almost every branch of industry. One of the main components in polyurethane synthesis are polyols, which play a significant role in building the certain structure of polymer [1,2]. In the recent years, there is a noticeable increase in research where compounds from chemical recycling or renewable resources such as vegetable oils and animal fats are applied [3–5]. The interests in such components is a result of European Union directives [6,7] related to limiting and recycling of waste and searching for new alternative raw materials. This is the step into the development of clean technologies so-called green chemistry that are using natural resources in cost effective manner and manufacture of these products will be held in order to minimise the amount of created waste.

During chemical recycling of polymer waste, the intermediates with the possibility of reuse are obtained but also the amount of landfilled waste is decreased [8,9]. Many researchers are applying obtained recycled polyols in polyurethane foam synthesis [10–13]. Polyol obtained from polyethylene terephthalate decomposition was used with 4,4-diphenylmethane diisocyanate to produce polyurethane foam [14]. Molero et al. applied, recovered polyol from glycolysis of polyurethane, up to 50% could be applied without relevant changes in rising profiles and the physical properties of the foams [15].

In our earlier work [16] glycolysates, obtained during polyurethane glycolysis by using difunctional hydroxyl compounds (1,4-buthanediol and polyethylene glycol), were applied in polyurethane synthesis as a chain extender. DMA results showed the higher content of glycolysate in chain extender mixture, the better polyurethane properties. In another our work [17] also the glycerolysate was applied into new polyurethanes as a part of the polyol component. Nonetheless, in the contrast to this paper, only the upper phase of glycerolysate was used and furthermore the glycerolysate was obtained from flexible polyurethane foam decomposition, while in this paper the used glycerolysates were obtained during polyurethane elastomer decomposition and moreover, the applied glycerolysates were single-phase.

In general, the satisfactory mechanical properties of PUs fall above 80 °C, and the thermal degradation starts above 200 °C. Thermal stability of material is affected



by the crosslinking which can occur in the subsequent stages due to the reaction of isocyanate groups with urethane or urea bonds and allophanate or biuret groups are formed. Increasing the concentration of polymer crosslinking can be achieved by increasing the functionality of the polyol, isocyanates and chain extender, ($f > 2$) or the use of a higher molar ratio [NCO]:[OH]. It is caused because more energy is needed to break additional bonds resulting from increased crosslinking density, before the disintegration of the entire network [20,21]. Therefore addition or replacement of commercial polyol with the one from recycling can result in the higher thermal stability of new material [17].

The aim of this study was to investigate the possible use of intermediates obtained by glycerolysis, which was detailed described in our the previous paper [20]. Glycerolysis of polyurethane elastomer waste was carried out using crude glycerine with 60% of purity derived from the biodiesel production. Obtained intermediates – called glycerolysates were used in the synthesis of polyurethanes, as a part of the polyol component. The glycerolysates were applied in similar polyurethane system which was used to produce the polyurethane elastomer, that was later recycled. Due to their reactivity, the phosphoric acid was added as an inhibitor of side reactions. The obtained materials products were tested to determine the effect of glycerolysate on the structure and properties of polyurethane.

2. Experimental

2.1. Materials and polyurethane synthesis

Intermediates obtained from glycerolysis of polyurethane elastomer were used in this study as a reactive polyol component, replacing part of commercial polyol. Glycerolysates used in this study were widely characterised in our paper [20]. The hydroxyl value of glycerolysate GL 4/1 and GL 10/1 is 240 and 163 mg KOH g⁻¹, respectively.

Recycled polyurethane elastomers based on a mixture of glycerolysate (GL) – reactive recovered intermediate and poly(ethylene-butylene)adipate diol as polyol component was synthesised by the prepolymer method under pressure in 0.5 dm³ glass reactor. The dried polyol (Polios 55/20, Purinova, OH_{number} = 58 mg KOH g⁻¹) and glycerolysate (GL 4/1 and GL10/1 described in a paper [20]) were first premixed for 30 min in different polyol/glycerolysate ratios (up to 20.% replacement of commercial polyol) and phosphoric (V) acid (H₃PO₄ 85% wt. in water, POCH Avantor, Poland) 0.5% on glycerolysate amount was added as side reactions inhibitor. After

that, the 4,4'-diphenylmethane diisocyanate (MDI, Interchemol, Poland) was added. The prepolymerisation step was carried out at 80 °C for 1,5 h under the vacuum. The percentage of the free NCO groups in prepolymer was equalled to 8 according to standard PN-EN 1242:2013-06 with a change of solvent from toluene to acetone. In the second stage, the 1,4-buthanediol (BD, Brenntag, Poland) was added to the prepolymer as a chain extender and stirred for 30 s. DABCO - 1,4-diazabicyklo[2.2.2]octane (Sigma-Aldrich) was used as the catalyst only for the reference sample. The molar ratio of [NCO]:[OH] was kept constant for all samples 1:1. All samples were moulded by gravity casting to the forms and then cured at 100 °C for 24 h. For comparison, a reference polyurethane without glycerolysate was synthesised.

The scheme of two steps synthesis of polyurethane obtained with a commercial polyol, glycerolysate, MDI and BD is shown in Scheme 1. The codes of polyurethane samples used in the study, hard segment content and degree of phase separation are given in Table 1.

Scheme 1.

2.2. Characterisation techniques

Spectroscopic analysis of polyurethane elastomers was carried out using an FTIR Nicolet 8700 spectrophotometer (Thermo Electron Corporation) and ATR technique. The Specac heated golden gate single reflection diamond ATR accessory was used, and it operated up to 200 °C. Spectra were registered at room temperature for wavenumbers ranging from 500 to 4500 cm^{-1} at 4 cm^{-1} nominal resolution with 64 scans.

Based on FTIR analysis, the degrees of phase separation (DPS) were calculated using the following equations [21]:

$$R = \frac{A_b}{A_f} \quad (1)$$

$$DPS = \frac{R}{R+1} \quad (2)$$

where R —carbonyl hydrogen bonding index; A_b — absorption intensity of hydrogen-bonded carbonyl; A_f —absorption intensity of free carbonyl. These values were taken from the bands in the range of 1640 – 1770 cm^{-1} , corresponding to the stretching vibration of the C=O group, by analysing the intensities of the carbonyl stretching

vibrations of free and hydrogen-bonded groups whose overlapping bands were located at 1728 and 1702 cm^{-1} .

Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC-7 equipment. PU samples with a weight between 5 and 10 mg were encapsulated in aluminium pans and were heated from -75 to 200 °C at a scanning rate of 20 °C min^{-1} under a constant nitrogen flow. The inflexion point of heat capacity change observed was chosen as glass transition temperature (T_g). Melting temperature (T_m) was settled as the maximum of endothermic peak taking the area under the peak as melting enthalpy (ΔH_m).

Thermogravimetric analysis (TGA) was performed with a Netzsch TG209 apparatus using 8 mg samples in the temperature range 35–600 °C and under a nitrogen atmosphere at a heating rate of 20 °C min^{-1} .

Dynamic mechanical analysis (DMA) of polyurethane elastomers was performed using DMA Q800 Analyzer (TA Instruments) according to ASTM D6045. Measurements were taken in a temperature range of -70°C to +150 °C at an operating frequency of 10 Hz and a heating rate of 4 °C min^{-1} . Approximate dimensions of samples were 40 mm × 10 mm × 4 mm (length × width × thickness).

Mechanical analysis in static condition was conducted with a tensile test (tensile strength (TS), elongation at break (ϵ_b), permanent elongation after break (ϵ_p) and performed using Zwick Z020 tensile testing machine. Dumbbell shaped samples with normalised dimensions by PN-ISO 37:1998 were tested. The cross-section of samples was 6.8 × 2.8 mm. The tests were executed at 200 mm min^{-1} rate. Measurements of the mechanical properties were carried out at the room temperature. The obtained results are reported as average values calculated from four samples.

Hardness was determined according to PN-EN ISO 868:2005 standard using an electronic durometer type A Zwick/Roell. Shore A durometer perpendicularly applied for 3 s.

3. Results and discussion

3.1. Structure characterisation

In Fig. 1 infrared spectra of chosen polyurethanes synthesised with glycerolysates and polyol mixture: Polios 100%, GL 4/1 (20%)+Polios 80%), GL 10/1 (20%) +Polios (80%) are shown. It is possible to observe two main vibration regions.



At 3330 cm^{-1} appears -NH groups stretching vibration, which increased as glycerolysates were incorporated. The other one is associated with carbonyl stretching vibrations $\nu\text{C=O}$ at wavenumber region $1727\text{-}1700\text{ cm}^{-1}$. Double peak of C=O is related with the absorbance of H-bonded carbonyl groups which appears at lower wavenumbers than of free urethane carbonyls [4]. The position of the hydrogen-bonded C=O groups was assigned to the 1701 cm^{-1} wavenumber and that of non-hydrogen-bonded C=O groups to the 1727 cm^{-1} wavenumber. The intensity ratio of the hydrogen-bonded to the non-hydrogen-bonded peaks is slightly higher for polyurethane synthesised with glycerolysate than for reference PU. Peaks appearing at 2966 and 2880 cm^{-1} are associated with stretching vibrations of methyl and methylene groups, whereas the deformation stretching of $\delta\text{C-H}$ can be found at 1415 cm^{-1} . Vibration bands at 1530 and 1309 cm^{-1} correspond to the νNH amine group in urethane bond and vibration of $\nu\text{C-N}$, respectively. The stretching vibrations in the region $1200\text{ - }1090\text{ cm}^{-1}$ indicate the presence of ester group [22].

Fig. 1

Based on Eqs. (1) and (2) the degree of phase separation was calculated in dependence on the amount of glycerolysate in polyurethane formulation and results are shown in Table 1. The formation of hydrogen bonds between the carbonyl groups and NH in the urethane groups leads to the creation of rigid domains and favours the process of micro-phase separation. When the hydrogen bonds start to form between the -NH groups and the C(O)O or C-O-C groups the latter being a structural element of elastic segments, the phase dispersion occurs [2]. DPS slightly increased with the presence of glycerolysate in polyurethane formulation. It is associated with the formation of more hydrogen bonds linking the rigid fragments which can indicate the increasing degree of physical crosslinking, and that is in correlation with the increasing hard segment content [23].

3.2. Thermal properties

Thermal transitions of PUs were analysed by differential scanning calorimetry as shown in Fig. 2 and Table 2, where the results of thermal transitions from first and second heating scan are summarised. The glass transition (T_g) occurs as a step increase in the heat capacity of the sample during the heating, which is due to an enhancement of molecular motion in the polymer [24]. T_g of the soft segment for all prepared samples is in the range from of -36 to $-18\text{ }^\circ\text{C}$ and -24 to $0\text{ }^\circ\text{C}$ in the first and



second heating scan, respectively. Initially, the addition of glycerolysate is shifting slightly the T_g to lower temperatures but with the higher incorporation of glycerolysate, the T_g is shifted to a higher temperature. 5% polyol replacement with glycerolysate does not influence much on glass transition temperature. However, the shift of T_g to higher temperatures can be related to higher branching or crosslinking of that polyurethane due to the presence of molecules with different chain length which influences on mobility polymer chain (Scheme 1).

Fig. 2

All polyurethanes showed multiple melting endotherms with the shoulder in the first scan but exhibited a broader endotherm in the second scan, performed right after the cooling cycle. Apart from the clear and visible step of glass transition, in the first heating scan, there can be distinguished for almost all samples three (or two) different endotherm peaks. Regions of this thermal activity are at about 70, 140 and 170 °C. The first region can be ascribed as dissociation of small unstructured hard segments. The second and/or third region can be identified to some domain region possessing a preferential chain ordering [1,25]. In the second heating scan, melting temperatures of the hard segment of synthesised polyurethanes are shifted to lower values as a higher content of glycerolysate is used. It is caused due to the higher restriction to hard segment ordering imposed by branched chains of glycerolysate.

The results from the thermogravimetric analysis are shown in Fig. 3 (TG curves) and Fig. 4 (DTG curves). Thermal stability of all prepared polyurethanes can be considered as good as the beginning of the mass loss starts above 300 °C as presented in Fig. 3. It can be stated that addition of glycerolysate improves thermal stability as the beginning of degradation starts at higher temperatures for polyurethanes containing either GL 4/1 or GL 10/1. However, decomposition of materials synthesised with GL 10/1 glycerolysate starts at slightly higher temperatures. It is in accordance to the thermal stability of glycerolysate itself, that shows better thermal properties with higher polyurethane to glycerine mass ratio [20]. Higher thermal stability of series PU-GL4/1 and PU-GL 10/1 can be associated with the more branched structure of polyurethane due to the probable branched structure of glycerolysate, what can assure better durability on temperature. The amount of residue is in the range approx. 4-8% and for polyurethane containing glycerolysate



that amount is higher possibly due to the presence of urethane oligomers and by-products in glycerolysate.

Fig. 3

All obtained materials indicate two stage thermal degradation which is typical for polyurethanes what can be seen in Fig. 4. The first stage at temperatures 331 – 341 °C is related with degradation of hard segments (urethane bond) and at temperatures 392-399 °C, the second with elastic segments (polyol part). Due to the presence of two peaks, it can be confirmed that prepared materials exhibited similar segmented structure. For reference sample, the second stage of degradation is the fastest than for other materials. The slowest decomposition rate executes PU-4/1-20 and PU-10/1-20, where the highest concentration of glycerolysate is applied. It can be related to the more branched structure of recovered polyol (including higher functionality) than for commercial polyol. Moreover, it can be noticed that the participation of degradation is on the favour of the hard segment to the soft segment with the usage of glycerolysate, especially with GL 10/1.

Fig. 4

3.3. Mechanical and thermo-mechanical characterisation

In Figs.5 – 7 the thermo-mechanical curves recorded during DMA tests are shown. The variations of storage modulus (E'), loss modulus (E'') and loss factor ($\tan\delta$) versus temperature are presented. The thermo-mechanical analysis is giving the information about flexible (soft) and rigid (hard) polyurethane blocks. The maximum E' (Fig. 5) values are registered at the lowest temperature and are in the range 3.2 to 3.7 GPa. Glycerolysate addition did not cause meaning changes in the storage modulus values. With rising temperature (in the range -30 to 20 °C), there is a sharp decrease in storage modulus values what suggests changes in the material properties and transition to the viscoelastic state. In that region, the glass transition can be determined from $\tan\delta$ peak (Fig. 6). After reaching 20°C temperature, the materials go to the rubbery state.

Fig. 5

The glass transition, estimated as a maximum peak of loss factor curve, for reference material and polyurethane with 5% replacement of commercial polyol is

similar, (-6.9 to -4.7 °C) (Fig. 6). The higher amount of recovered polyol in polyurethane formulation causes shifting T_g to higher temperatures (above 0 °C). This behaviour is related, as was already shown in DSC curves, with higher restriction of molecules movement due to the more branched structure of glycerolysate than of neat polyol and simultaneously resulting in the more crosslinked structure of these materials [26]. However, the higher usage of glycerolysate GL 4/1 affected more the material properties, so it is possible that this glycerolysate caused higher crosslinking of polyurethane.

Fig. 6

The obtained polyurethanes exhibit similar values of the loss factor, which is in the range of 0.39-0.45. In a physical sense, E' is related to the stiffness of the material and the loss modulus (E'') is reflected in the damping capacity of the material [27]. E'' values (Fig. 7) for all prepared PUs are in the range 260-380 MPa, but for polyurethanes obtained with glycerolysate, E'' indicates a bit lower values. This can be considered as an advantage of using glycerolysate due to less energy is lost [28].

Fig. 7

In Table 3 the results from static mechanical properties derived from tensile test and hardness are summarised. The highest tensile strength was observed for reference polyurethane and PU-GL 4/1 with 5% replacement of polyol. The usage of higher glycerolysate content in polyurethane formulations is causing a decrease in tensile strength and elongation at break for obtained materials, especially when glycerolysate GL 4/1 is applied at higher concentration. Better mechanical properties show PU-GL 10/1 series where the tensile strength is above 22 MPa, what can be considered as a good result [17]. It can be associated with the properties of applied glycerolysate itself, as it is a mixture of few different compounds with various functional groups and molecular weight [20], as it was shown in Scheme. 1. Incorporation of glycerolysate to the system is causing the decrease in the chain mobility, confirmed by shifting T_g to higher temperatures, simultaneously resulting lower elongation at break. Permanent elongation is a very important parameter which characterises returning the material to its original state. For reference sample that value is ca. 38% and for polyurethanes, with glycerolysates, these values are lower



(from 2 to 23%) and is a favourable phenomenon. Hardness is similar for all polyurethanes in the range from 81 to 89 °ShA. However, obtained cast polyurethane materials are comparable and even exhibit better properties than these described in the literature for similar materials [29].

4. Conclusions

The reactive glycerolysates, intermediates from polyurethane elastomer chemical recycling, were mixed with a commercial polyol (Polios 55/20), MDI and 1,4-buthanediol as chain extender to produce cast polyurethanes. As glycerolysate is a mixture of different compound with various chain lengths, with higher incorporation it causes branching or crosslinking polyurethanes due to the presence of some three functional structures in glycerolysate. Glass transition determined by DSC in second heating scan was in the range -24 to 0 °C, increasing with higher glycerolysate content, but still characteristic low for polyurethanes materials. All prepared polyurethanes are thermally stable until ca. 310 °C, regardless glycerolysate type and concentration. Thermal decomposition takes place in two stages, the first ca. at 330-340 and the second 390-400 °C, however, the share of hard segment decomposition with the incorporation of glycerolysate is changing. Thermo-mechanical properties in the dynamical mode were satisfying exhibiting storage and loss moduli were in the range from 3.5 to 3.69 GPa and from 264 to 380 MPa, respectively. Replacement of commercial polyol by 5% of recovered polyol did not result in worsening of mechanical properties, and the tensile strengths were approx. 26-32 MPa. Higher replacement caused a decrease in tensile properties and elongation at break values. Such prepared materials can find application in the production of couplings, external and internal body parts of the cars or shoe soles.

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Table 1. Designation of samples, chemical composition, hard segment content (HS) and degree of phase separation (DPS).

Table 2. Thermal transitions values from first and second heating scan of the synthesised polyurethanes.

Table 3. Static mechanical properties (tensile strength - TS; elongation at break - ϵ_b , permanent elongation after break - ϵ_p) and hardness of prepared polyurethanes.

Table 1. Designation of samples, chemical composition, hard segment content (HS) and degree of phase separation (DPS).

| Code | Chemical composition | GL in respect to polyol (%) | HS (%) | DPS (%) |
|------------|-----------------------|-----------------------------|--------|---------|
| PU-REF | POLIOS:MDI:BD | - | 37 | 42 |
| PU-4/1-5 | POLIOS+GL 4/1:MDI:BD | 5 | 40 | 45 |
| PU-4/1-10 | | 10 | 41 | 45 |
| PU-4/1-20 | | 20 | 45 | 46 |
| PU-10/1-5 | POLIOS+GL 10/1:MDI:BD | 5 | 39 | 48 |
| PU-10/1-10 | | 10 | 40 | 47 |
| PU-10/1-20 | | 20 | 42 | 46 |

Table 2. Thermal transitions values from first and second heating scan of the synthesised polyurethanes.

| Sample | T _g (°C) | T _m (°C) | ΔH _m (J g ⁻¹) |
|------------|---------------------|---------------------|--------------------------------------|
| PU-REF | -30 (-23) | 75/163 (199) | 0.6/8.1 (1.5) |
| PU-4/1-5 | -36 (-20) | - /167 (197) | - /15.2 (1.8) |
| PU-4/1-20 | -18 (0) | 69/147/177 (132) | 0.6/2.0/3.4 (1.4) |
| PU-10/1-5 | -30 (-24) | 76/132/177 (168) | 1.1/0.7/7.7 (2.2) |
| PU-10/1-20 | -22 (-2) | 75/138/179 (157) | 0.7/1.3/6.2 (1.4) |

*Data in parenthesis correspond to the second heating scan. Peaks of multiple endotherms processes are separated by bars.

Table 3. Static mechanical properties (tensile strength - TS; elongation at break - ϵ_b , permanent elongation after break - ϵ_p) and hardness of prepared polyurethanes.

| Sample | TS (MPa) | ϵ_b at break (%) | ϵ_p after break (%) | Hardness (°ShA) |
|------------|----------|---------------------------|------------------------------|-----------------|
| PU-REF | 35.6±2.9 | 713 ±43 | 37.7±5.6 | 89.1±0.7 |
| PU-4/1-5 | 32.8±1.9 | 591±36 | 28.1±4.3 | 88.4±1.3 |
| PU-4/1-10 | 14.8±1.2 | 191±21 | 2.2±1.5 | 86.9±1.6 |
| PU-4/1-20 | 14.9±1.3 | 161±8 | 23.0±0.8 | 87.9±1.4 |
| PU-10/1-5 | 26.3±1.3 | 573±18 | 21.6±1.2 | 80.9±2.3 |
| PU-10/1-10 | 23.1±2.5 | 463±71 | 23.1±5.4 | 82.3±1.2 |
| PU-10/1-20 | 22.0±0.5 | 300±9 | 7.1±0.8 | 87.1±1.0 |

Scheme 1. Scheme of two steps polymerisation of polyurethane. The first step is prepolymerisation and second step is an extension of prepolymer chain. The proportions of each component can vary.

Fig. 1. FTIR spectra of synthesised polyurethanes without and with different glycerolysates.

Fig. 2. DSC thermograms of prepared polyurethanes, a) first heating scan, b) cooling scan, c) second heating scan.

Fig. 3. TG curves obtained for the PU samples.

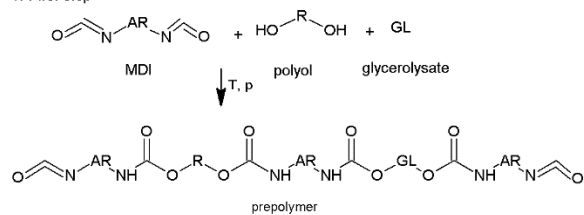
Fig. 4. DTG curves obtained for the PU samples.

Fig. 5. Storage modulus (E') as a function of temperature for synthesised polyurethanes.

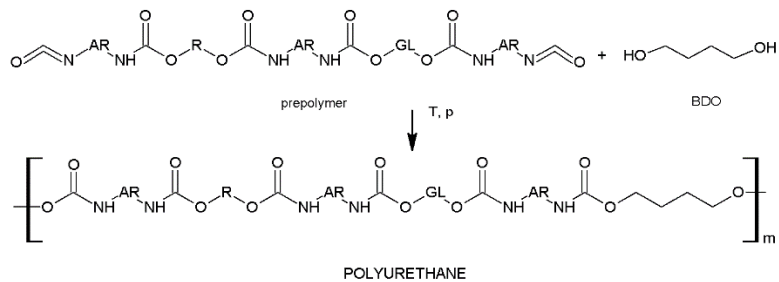
Fig. 6. Loss factor ($\tan\delta$) as a function of temperature for synthesised polyurethanes.

Fig. 7. Loss modulus (E'') as a function of temperature for synthesised polyurethanes.

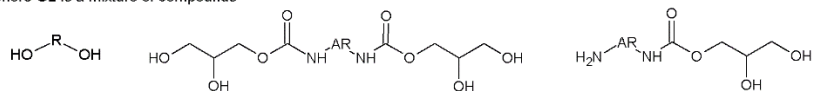
1. First step



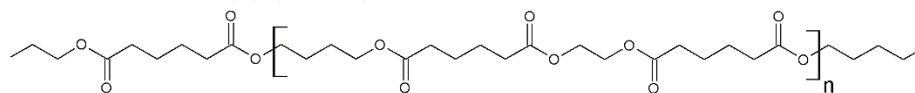
2. Second step



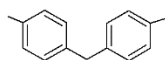
where GL is a mixture of compounds



where R is a linear structure from polyol (Polios 55/20)



where AR is an aromatic structure from MDI



Scheme 1.

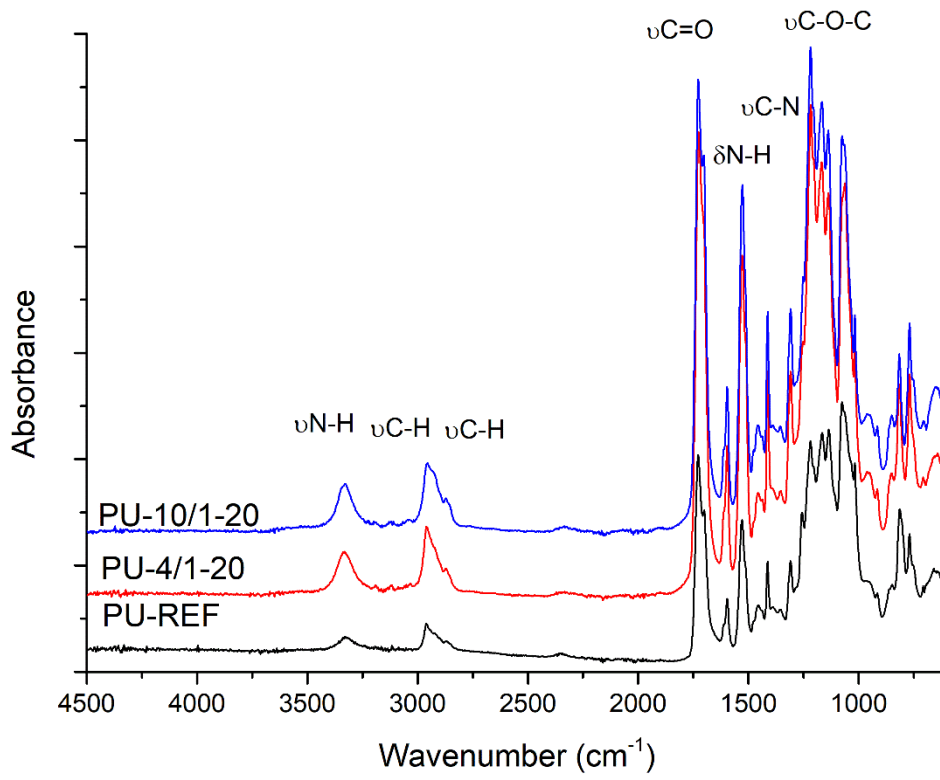


Fig.1

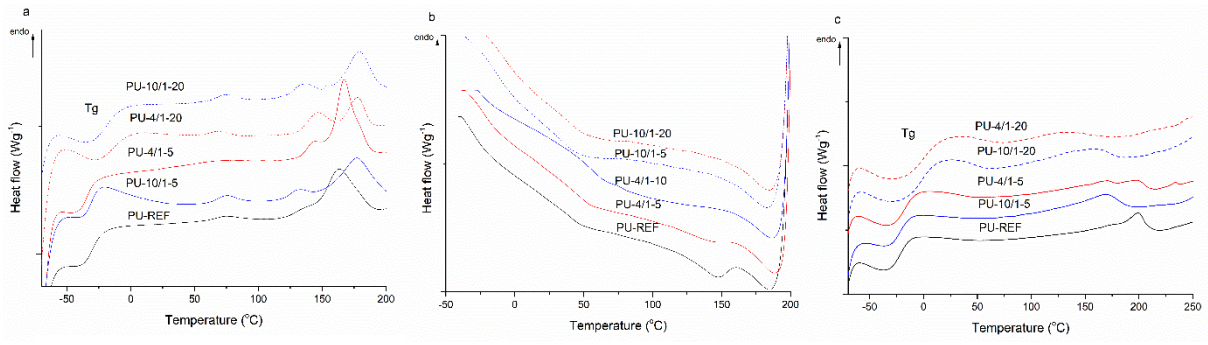


Fig.2.

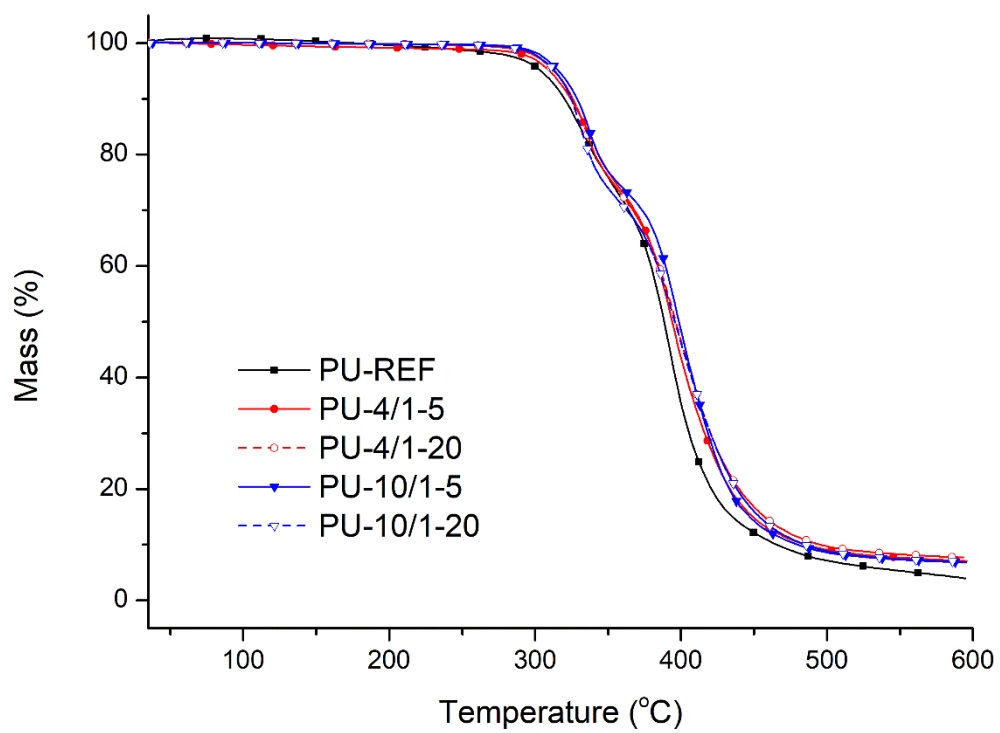


Fig.3.

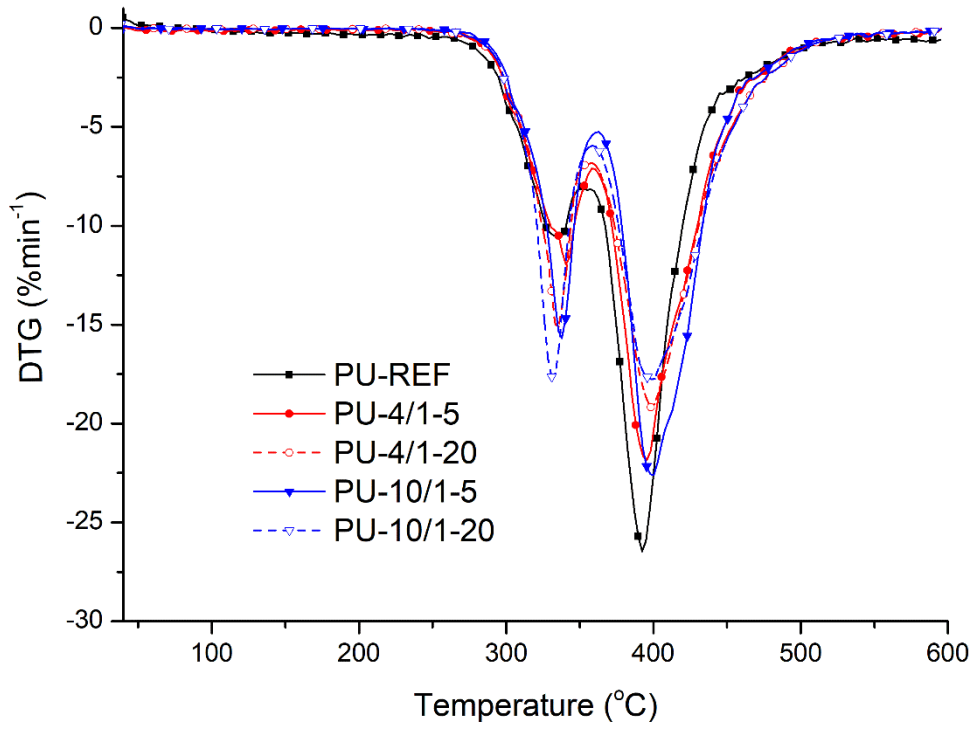


Fig.4.

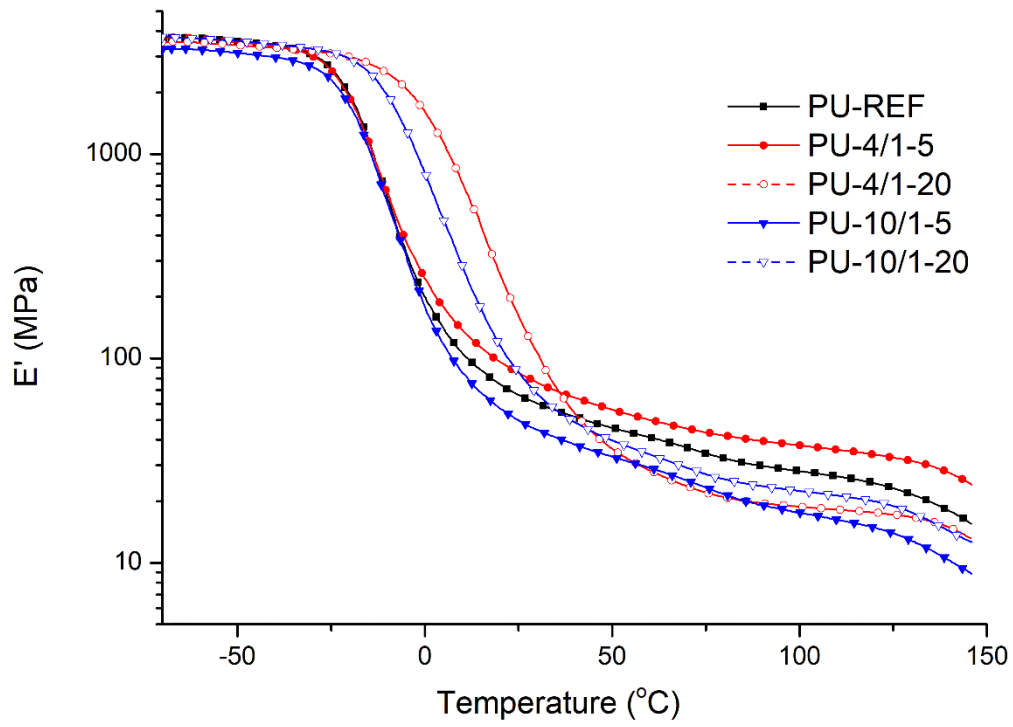


Fig.5

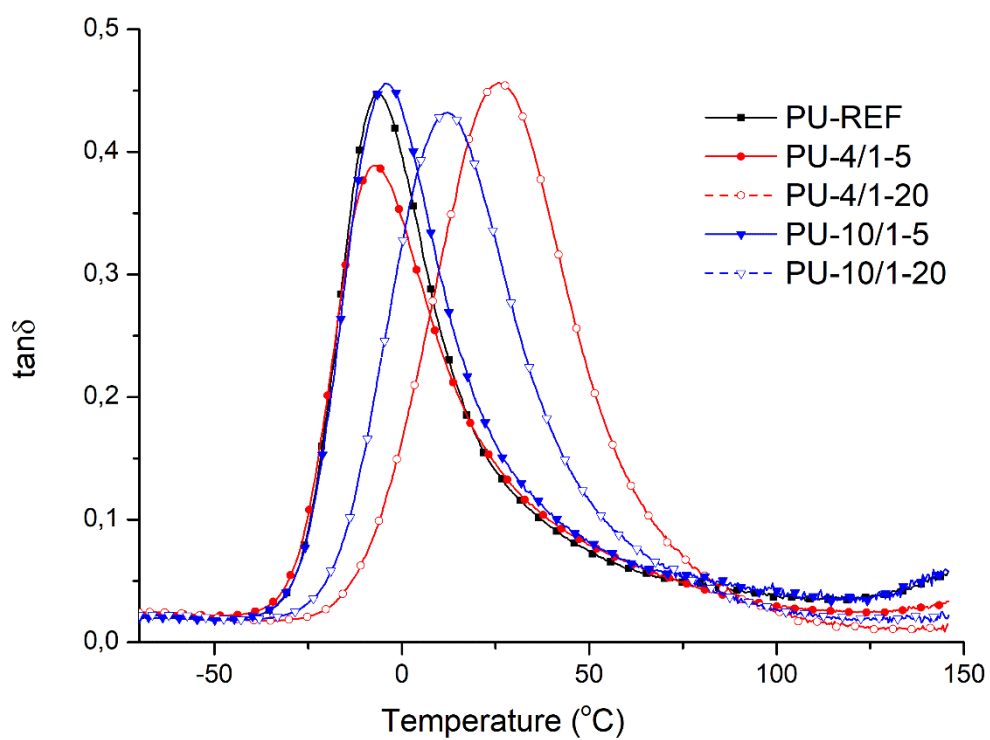


Fig.6

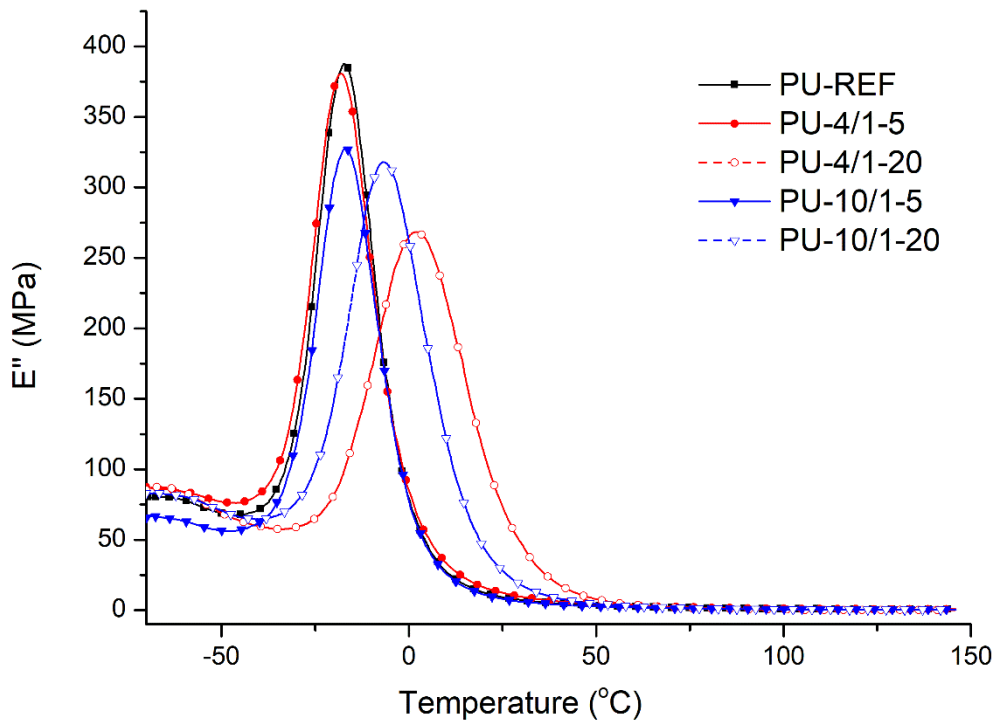


Fig.7